Effect of Steam Explosion Pretreatment Method in Pulp Production on Pilot Scale

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Abstract— The study on pulp production at a pilot scale and the implementation of steam explosion pretreatment in the process. The pulp production using the physic-chemical process that includes steam explosion pretreatment and mild alkaline treatment. The physicochemical and morphological characteristics, elemental composition and size distribution of the fiber were characterized using the scanning electron microscope (SEM), thermogravimetric analysis (TGA), X-ray Diffraction (XRD) and Fourier transform infrared (FTIR). The difference on the morphology of the raw and exploded can be clearly seen when the smooth structure of raw fiber turn ruptured and the size decreases from 213.6µm to 9.5µm. FTIR and TGA analysis provided clear evidence from the peak of lignin and hemicellulose were decreasing from the raw to the exploded fiber and pulp. The crystallinity of the fiber changes when treated. Thus, pulp can be produced in a large scale by using the steam explosion treatment.

Keywords— EFB; Pulp; Steam explosion treatment; Pilot scale; Characterization

1. INTRODUCTION

Lignocellulosic biomass is one of the most abundant and low cost renewable resource available in Malaysian and has a great potential of bio-fuel and chemical derivatives [1]. Lignocellulosic biomass usually comprised of lignin, hemicellulose, and cellulose. Cellulose is aligned parallel to each other in fibrils, which are surrounded by a matrix of lignin and hemicellulose. In order to produce the designated product, effective pretreatment is required to disrupt the this complex and heterogeneous matrix [1].

In recent years, Malaysia's largest solid lignocellulosic biomass contributor comes from the oil palm industries [2]. Lignocellulosic biomass produced from the oil palm industries which are the oil palm trunks, oil palm fronds, empty fruit bunch (EFB) and palm pressed fibers [3]. EFB as an oil palm biomass product attracted interest among researcher due to its cellulosic content, and easy to obtain. A few years back, EFB was a valueless biomass produced from the oil palm mill and it will casually be thrown back to the oil palm plantation or burnt in the incinerators for it ash. Abdullah and Sulaiman stated in 2013, EFB has a huge potential but currently being wasted.

With the current raw material for the production of pulp and paper. The industry is facing a serious problem due to raw material shortages. While wood is the main resource, there are plenty lignocellulosic biomass that can be applied for pulp production. However, problems encountered in the pretreatment of this lignocellulosic biomass,

Pretreatment is an important step to deal with lignocellulosic biomass complex structure by rupturing its structure and making it easier to be digested throughout the process [4]. Until now, many have develop several type of pretreatment method such as biological, physical, chemical, physiochemical and combination of several method [5,6,7,8]. I most cases, removing of lignin and hemicellulose, plant cell wall structure disruption, and increase the surface area are the primary target of the pretreatment [9,10,11].

From the developed technology for the pretreatment of lignocellulosic biomass, steam explosion in which can be categorized in the physic-chemical process. This is because the process itself involving high pressurizes saturated steam and a sudden decompression of the system causing the biomass fiber to rupture and release of organic acid that triggered the autohydrolyzing of hemicellulose and depolymerization of the lignin [12]. Steam explosion has been adapted on the pretreatment of lignocellulosic biomass more regularly due to its promising improvement in enzymatic digestibility or solvent accessibility [13]. Steam explosion also will greatly decrease the chemical consumption for further treatment and has low energy consumption value.

The aim of this study was for pulp production using the steam explosion treatment and other treatments that was hot water treatment and mild alkaline treatment using 5% sodium hydroxide (NaOH) in a pilot scale production line. The characteristic and changes of the pulp was characterized throughout the process using scanning electron microscope (SEM), thermogravimetric analysis (TGA), X-ray Diffraction (XRD) and Fourier transform infrared (FTIR)

2. MATERIALS AND METHOD

A. Material

Empty fruit bunch (EFB) was obtained from LKPP Corporation Sdn. Bhd. palm oil mill, Lepar, Pahang. 99% industrial grade caustic soda (NaOH) obtained from the local vendor Kong Long Huat Chemicals Sdn. Berhad.

B. Sample preparation

EFB was dried at room temperature for 1 week. Then the EFB was ground using the SIMA grinder model FG 400×200 equipped with 200 mm mesh.

C. Pulp production

Production of pulp was performed at a Cellulose Pilot Plant located at Lepar, Pahang.

D. Steam explosion treatment

Steam explosion treatment of EFB was carried out using the pilot plant 700-L pressure vessel. Saturated steam was provided by the LCSB oil palm mill. Grounded EFB were weighed and loaded into the pressure vessel. Saturated steam was supplied into the pressure until the pressure of the vessel reached 20 bar and the countdown for the steam explosion started. When the countdown ended the blowdown valve was opened and the sudden release of pressure created the steam explosion. Exploded EFB fiber was collected in the collecting tank and transferred into the first mixing tank.

E. Hot water treatment

Hot water treatment was carried out using a 1000L jacketed mixing tank equipped with an overhead stirrer. The transferred exploded fiber was mixed with water at 1.25% consistency. The mixing tank was heated using low pressure steam until the desired temperature, 80°C was reached. After 1 hour of mixing, the slurry solution was filtered using a cotton bag and transferred into the second mixing tank for mild alkaline treatment.

F. Alkaline treatment

Alkaline treatment also using the 1000L jacketed mixing tank equipped with an overhead stirrer. 5% NaOH solution was prepared and heated to 80°C. Then hot water treated fiber was transferred into the tank and stirred for 1 hour. After 1 hour the produced pulp was filtered using the cotton bag and washed using deionized water until the pH reached 6.5-7.5. Then the produced pulp was dried at 80°C in an oven for 12 hours.

G. Characterization

H. Determination of fiber consistency

Fibers were dried in the oven at 105˚C for 2 hours before being weight using analytical balance. The calculation for consistency of the fiber for the synthesis was done using equation (1).

$$\frac{oven\ dry\ weight\ of\ pulp}{weight\ of\ pulp+water} \times 100\% \quad (1)$$

I. The thermogravimetric analysis (TGA)

The thermogravimetric analysis (TGA) of raw, exploded fiber and pulp were analyze using the TGA Q500 by TA Instruments. TG and DTG curves were obtained under a dynamic atmosphere of synthetic air (flow rate of 35 mL min^{-1}) heating rate of 10 °C min^{-1} from 30 to 900 °C.

J. Fourier transform infrared (FTIR)

The Infrared (IR) spectroscopy of the produced pulp was performed between bands 4000 to 500 cm^{-1} using The Nicolet iS50 FT-IR Spectrometer. The tests were carried out on the raw EFB, steam exploded fiber and the produced pulp.

K. Surface morphology

The scanning electronic microscopy (SEM) was carried on a FEI Quanta 450 under 1-15-kV was used to analyze the morphology of raw and exploded fiber. The morphology of sample is performed with difference magnification using scanning electron microscope (SEM). Samples were mounted on aluminium stubs. The average length and diameter of fiber were calculated using a digital image analysis, Image J software.

L. X-ray Diffraction (XRD)

The crystallinity of the raw, exploded fiber and pulp were monitored using Broker D8 Advance X-ray diffractometer (XRD) with Ni-filtered CuKα radiation. The test samples are scanned with in 2θ angle range from 5°to 60°at 2 per minute. The crystallinity index Crl value is calculated using the following Equation (2):

$$Crl(\%) = \frac{I_{002} - I_{am}}{I_{002}} \times 100\% \quad (2)$$

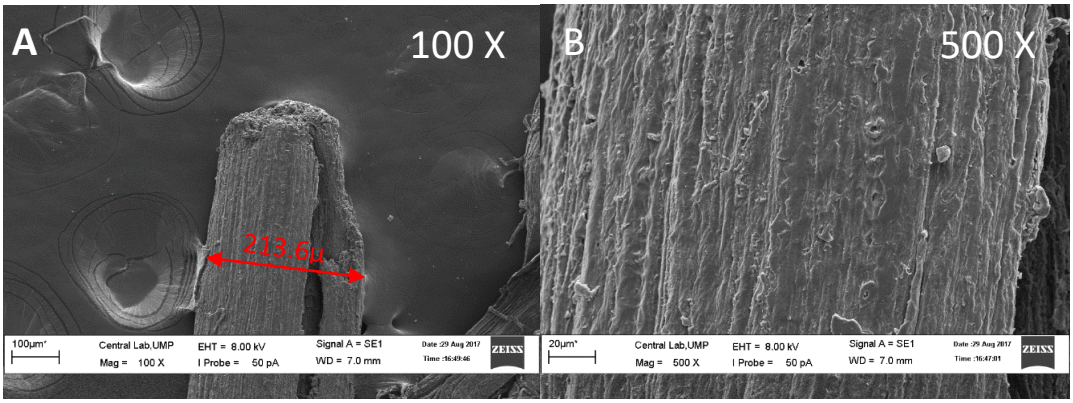
Where the I_{002} is the maximum intensity of the (002) lattice diffraction peak and I_{am} is the intensity scattered by the amorphous part of the sample. The mean size of crystalline region was evaluated to show the changes in the crystalline structure and was calculated using the Debre-Scherrer Equation (3):

$$D = \frac{\kappa\lambda}{\beta cos\theta} \quad (3)$$

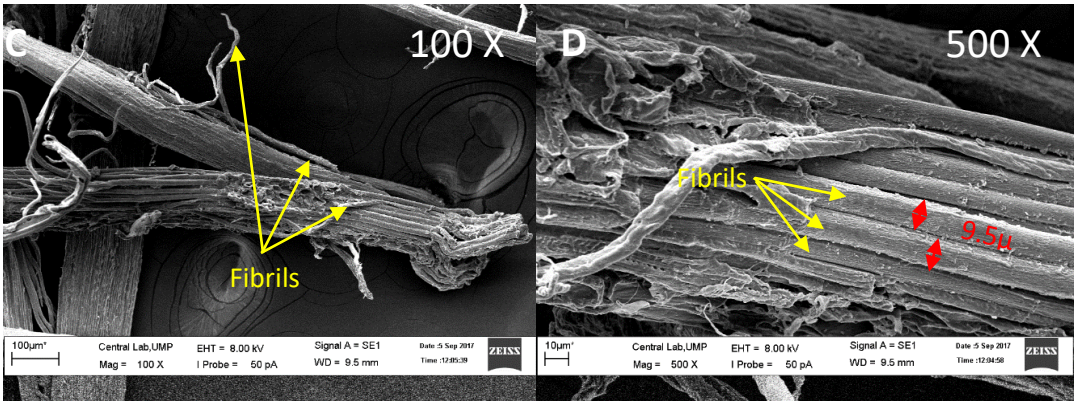
3. RESULT AND DISCUSSION

A. Surface morphology analysis

The effects of steam explosion treatment on the morphology of the fiber were observed using the SEM at 100x and 500x magnification. Figure 1 shows the morphology of the raw fiber (Figure 1A and 1B), show a long smooth fibril with a diameter of 213.6 µm. On the contrary, the steam exploded fiber show that the fiber was ruptured and the fibril began to individualized (Figure 1C and 1D) and the mean for the fibrils are diameter 9.5 µm. Steam explosion treatment had led to changes in morphological smooth structure and size of the raw fiber to a ruptured structure and decrease in size of the fibrils. During the steam explosion treatment, the saturated steam will penetrates into fiber through high vapor-phase diffusion and condensate to form liquid water inside the fiber. But at the end of the treatment when sudden release of pressure occurs, water inside biomass fiber will evaporates and explosion occur inside the biomass fiber causing the breakdown of the lignocellulosic structure of the fiber [11,13].



Raw Fiber (A and B)



Exploded fiber (C and D)

Figure 1: SEM micrographs of raw fiber (A & B) and exploded fiber (C & D) at a magnification 100x and 500x.

B. Chemical composition

The effect of steam explosion pretreatment at 10 min retention time on the chemical composition of the fiber was evaluated using the FTIR spectroscopy. The normalization of the FTIR peak was done by the peak (950-1200 cm^{-1}) with maximum at 1034 cm^{-1} with respect to the cellulose ring in which attributed to the C-O-C stretching of pyranose ring. Figure 1 shows the spectra for all the fiber showing similarities in spectra pattern indicating the chemical composition of the fiber remain unchanged throughout the process. The infrared spectra can be separated into two regions that are the low wavenumber in this case the finger print part (400-1800 cm^{-1}) and at high wavenumber which are -OH and CH stretching vibration [14].

From the figure 2, it can be observed that spectra of exploded fiber and pulp showing a decrease in peak (downward arrow) after the treatment. The peak at the O-H stretching and bending vibration which are the hydrogen bonded hydroxyl (OH) group of cellulose and absorbed water [14,15]. The decrease in the spectra was indicating that the hydrogen bonded hydroxyl was broken or ruptured during treatment [16]

The peaks in the finger print region which are the 1734 cm^{-1} is indicating to the C=O stretching of the acetyl and easter bond; 1612 cm^{-1} to 1508 cm^{-1} are referring to the C=C aromatic ring and C=H vibration of lignin; 1375 cm^{-1} are to the C-H deformation of cellulose and lignin; 1234 cm^{-1} are correspond to the axial asymmetric strain of =C-O- in ether, ester, and phenol group of lignin; and lastly the 1108 cm^{-1} and 1033 cm^{-1} are attributed to C-O stretching and C-H rocking vibration of cellulose [14,15,16,17]. The decrease of the spectra peaks on the low and high wavenumber region were attributed to breakage of the linkages of the bonds that linkages to the carboxylic group further indicating that both the steam explosion and alkaline treatment have causes the breakage of bonds and the hydrolysis of the hemicellulose fraction and de-polymerization of lignin components from the lignocellulosic structure of the EFB fiber [16]. Hemicellulose and lignin had been partially removed during the pulp production.

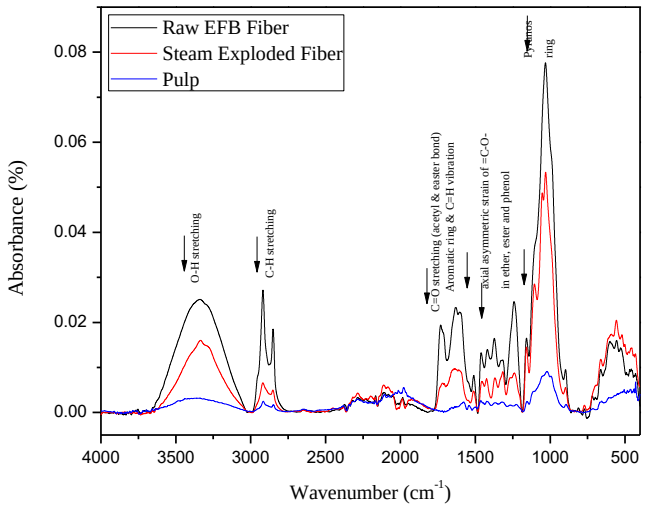


Figure 2: Fourier Transform Infrared (FTIR) spectra of raw, exploded fiber and pulp.

C. Crystallinity

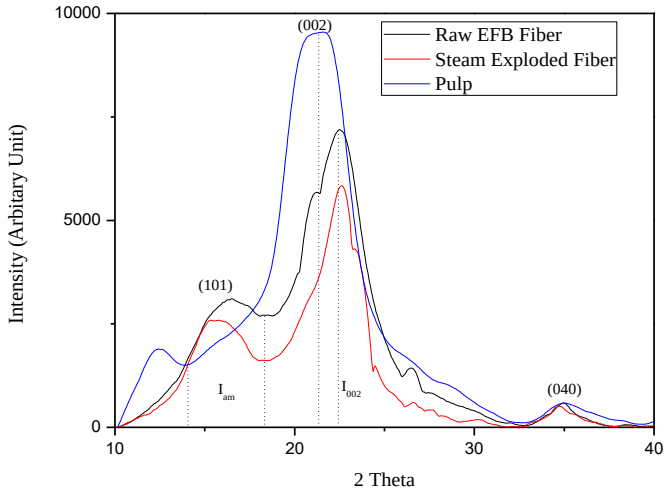


Figure 3: Crystallinity of raw, exploded fiber and pulp

The comparison X-ray diffraction patterns of raw, exploded fiber and pulp are presented in Figure 3. The 110 and 200 cellulose crystallographic planes are found at peaks 22° and 15° for all samples are associated with the crystalline structure in cellulose I. The crystallinity index of the fiber increases from 69.48% to 72.39% after the steam explosion treatment and further increases to 85.36% after the alkaline treatment. But for the crystallinity domain size of the fiber it increases from 2.11 nm to 2.36 nm after the steam explosion treatment but decreases after alkaline treatment to 2.02 nm. This shows that when the steam explosion occurs the organic acid produced had penetrates and hydrolyzed the amorphous region of the fiber and alkaline treatment further hydrolyzed the amorphous structure causing the cleavage of the glycosidic bonds and the releasing of individual crystallites [14,16]. The removal of the amorphous region cases the intermediate crystalline region to rearrange changing the domain size of the crystalline [16]. Table 2 show the crystallinity index and crystalline domain size of raw, exploded fiber and pulp.

Table 2: Degree of crystallinity index and crystalline domain size raw, exploded fiber and pulp

Sample	Crystallinity index (%)	Crystallinity domain size (nm)
Raw	62.48	2.11
Exploded fiber	72.39	2.36
Pulp	85.36	2.02

D. Thermogravimetric analysis

Figure 4 show the thermogravimetric analysis on the raw, exploded fiber and pulp. From the graph, it can be seen small fraction of weight loss before 120˚C were mainly due to moisture within the fiber evaporated and low molecular substances. [18]. it has been seen that the raw, exploded fiber and pulp start to decompose at an almost similar temperature. The onset temperature is the beginning of weight loss while the final temperature is the end of degradation. It was found that the decomposition of raw started at 218℃ and completed at 325℃ while exploded fiber started to decompose at 234℃ and completed as 330℃ and for pulp started decomposition at 260℃ and completed at 336℃. Based on the result obtained, the degradation of the raw is the slowest followed by the exploded fiber and pulp. This change in behavior can be attributed by the removing of the hemicellulose and lignin throughout the process of pulp production [18]. This process also shows that the process does slightly change the thermal stability of the fiber and confirmed that the produced pulp has a high thermal stability.

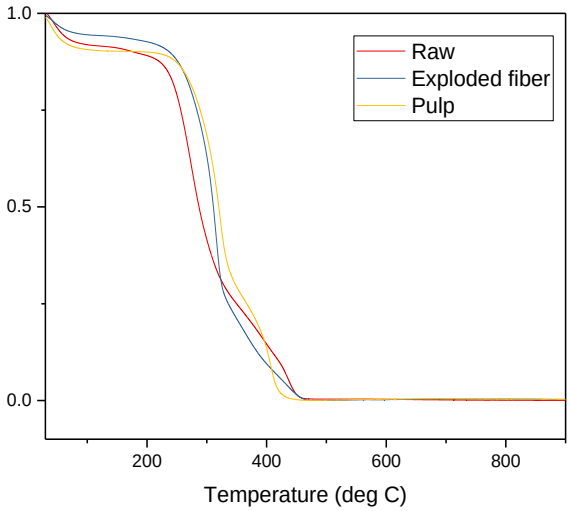


Figure 4: TGA curve of raw exploded fiber and pulp

4. CONCLUSION

Pulp has been successfully produced in a pilot scale. The integration of steam explosion pretreatment has improved the process by improving the other treatment by increasing the surface area of the fiber. The results obtained from FTIR and TGA analysis confirmed that hemicellulose and lignin structure has been successfully removed from the fiber. TGA analysis also shows the produced fiber has a high thermal stability. Furthermore, XRD show that the crystallinity of the fiber increase slightly from 69.48 to 72.39% after the steam explosion and further increases to 85.36% after the alkaline treatment.

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